

## **Release Agent for Non-Substrate Liquid Crystal Display**

### **BACKGROUND OF THE INVENTION**

#### **FIELD OF THE INVENTION**

The present invention relates to a release agent for non-substrate liquid crystal display which is applied to the assisting substrates in the process of non-substrate liquid crystal display so that the assembled liquid crystal display element can be separated from the assisting substrates and a non-substrate liquid crystal display element is obtained.

#### **DESCRIPTION OF THE RELATED ART**

The application of flat panel display (FPD) has helped reduce the weight and volume of display. The currently available liquid crystal display (LCD) technologies employ passive scan or active matrix to display images, which however requires considerable thickness stability for precision control. Otherwise even slight deformation will lead to serious image distortion. To bring about thinner and more impact-resistant FPD, some of the FPD technologies for conventional glass substrate process have shifted focus to the R&D of plastic substrate. The development of flexible FPD has brought FPD to a new prospect in terms of thinness, impact-resistance and ease of carriage.

As for the substrate of flexible FPD, plastic materials have received the most attention for their characteristics of being lighter, thinner, more impact-resistant, mobile, and easy to carry. But in processes with temperature of 200°C or higher, plastic material is

prone to deformation or even decomposition, hence limiting its dimensions and applications. To bypass the shortcomings of plastic substrate, non-substrate FPD is expected to be the process that draws the focus attention.

5 The patent of Philips entitled Liquid Crystal Display Laminate and Method of Manufacturing Such filed with WIPO (WO02/42832 A2) and published in Nature in 2002 reveals a process for single substrate LCD. The process employs UV radiation to produce polymerization and at the same time form polymer-covered liquid crystal with PSCOF (phase separated composite organic film) structure, which maintains uniformity on curved screens.

10 In the efforts to develop lighter and thinner non-substrate flexible FPD with greater design flexibility, release agent is one of the key materials and technologies for the new process. For release agent used in non-substrate flexible FPD process, the drawbacks of plastic material, including poor resistance to high temperature and being prone to deformation can be overcome. The formulation of release agent can also be adjusted to  
15 give it good and uniform releasability. Such release agent may be used in non-substrate liquid crystal display process and the LCD fabricated thereof can be applied in mobile phones and PDA in the near future. In essence, this is new technology for PC and communication equipment makers in the development of personal mobile electronic reading system.

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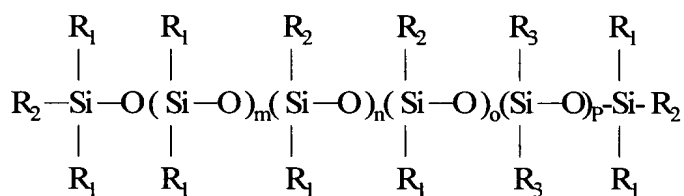
## **SUMMARY OF THE INVENTION**

The present invention discloses a release agent for non-substrate liquid crystal display element, comprising (a) 2-20 wt% of compounds selected from the group consisting of silicone, fluorine compounds and mixtures thereof; and (b) 0.5-30 wt% (based on the weight of (a)) of release modifier. The release agent is applied to the assisting substrates in the process of non-substrate liquid crystal display, so the assembled liquid crystal display element can be separated from the assisting substrates and a non-substrate liquid crystal display element is acquired.

Preferably the aforesaid release agent comprises (a) 3-7 wt% of compounds selected from the group consisting of silicone, fluorine compounds and mixture thereof; and (b) 3-20 wt% (based on the weight of (a)) of release modifier.

The aforesaid release modifier is a silicone modifier.

The aforesaid silicone modifier is a silicone compound having the following linear molecular structure:

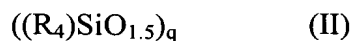


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wherein  $R_1$  is  $C_{1-3}$  alkyl;  $R_2$  is hydrogen atom,  $C_{1-3}$  alkyl or  $C_{2-10}$  alkenyl;  $R_3$  is  $C_{1-3}$  alkyl or phenyl; the aforesaid silicone compound has molecular weight of 3,500 ~ 30,000; if calculated by molecular weight,  $(-Si(R_1)(R_1)O-)_m$  accounts for 60 ~ 95% of the silicone compound,  $(-Si(R_1)(R_2)O-)_n$  accounts for 0 ~ 10%,  $(-Si(R_1)(R_2)O-)_o$  accounts for 0 ~ 10%,

and  $(-\text{Si}(\text{R}_3)(\text{R}_3)\text{O}-)_p$  accounts for 0 ~ 10%.

The aforesaid silicone release modifier may also be a compound having the following cage molecular structure:



5 wherein  $\text{R}_4$  is hydrogen atom or  $\text{C}_{2-10}$  alkenyl; and  $q$  is an integer from 8 to 16.

The higher the proportion of alkenyl group in the aforesaid release modifier, the easier the release following the application of release agent.

The aforesaid release agent can further comprise a catalyst which comprises platinum catalyst, sulfuric acid, hydrochloride acid, or acetic acid.

10 The aforesaid release agent can further comprise a proper solvent which comprises toluene, n-heptane, methylethyl ketone or composition thereof.

The aforesaid release agent can further comprise proper amount of inhibitor, such as alkynol compound or peroxide compound to enhance the operation life, i.e. pot life of release agent after mixture.

15 The aforesaid release agent can further comprise proper amount of microparticles, such as nanometer grade  $\text{SiO}_2$ ,  $\text{TiO}_2$  or organic polymer particles.

The aforesaid assisting substrate comprises glass, wafer, Teflon, ceramic or polymer substrate.

20 The release agent of the present invention is used in the process of non-substrate liquid crystal display to help the separation of assisting substrates from display element to obtain a non-substrate display element. The aforesaid release agent is a key material in the

new non-substrate liquid crystal display process, which breaks away from the traditional mode where liquid crystal display element is invariably affixed to a substrate. This new process overcomes the drawbacks of liquid crystal display element being unable to bend for it relies on the support of substrate or plastic substrate being prone to deformation under high temperature. It helps realize the goals of lighter, thinner and more flexible liquid crystal displays.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 illustrates the flow chart for the fabrication of first assisting substrate.

10 Figure 2 illustrates the flow chart for the fabrication of second assisting substrate.

Figure 3 illustrates the flow chart for the fabrication of non-substrate display element.

## **DETAILED DESCRIPTION OF THE INVENTION**

15 The present invention discloses a release agent for non-substrate liquid crystal display element, comprising: (a) 2-20 wt% of compounds selected from the group consisting of silicone, fluorine compounds and mixtures thereof; and (b) 0.5-30 wt% (based on the weight of (a)) of release modifier. The release agent is applied to the assisting substrates in the process of non-substrate liquid crystal display, so the assembled liquid crystal display element can be separated from the assisting substrates and a non-substrate liquid crystal display element is acquired.

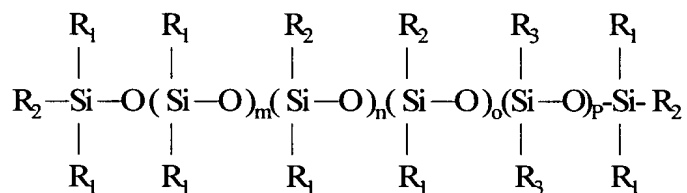
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Preferably the aforesaid release agent comprises of (a) 3-7 wt% of compounds selected from the group consisting of silicone, fluorine compounds and mixture thereof; and (b) 3-20 wt% (based on the weight of (a)) of release modifier.

5 The aforesaid silicone is a silicon polymer which contains Si-H and Si-CH=CH<sub>2</sub>, with the molar ratio of Si-H to Si-CH=CH<sub>2</sub> between 1.2 and 4.8, preferably between 2.0 and 3.5, and with molecular weight of between 100,000 and 1,000,000, preferably between 300,000 and 700,000. The aforesaid fluorine compound comprises Teflon, silicon fluoride, and fluothane.

The aforesaid release modifier is a silicone modifier.

10 The aforesaid silicone modifier is a silicone compound having the following linear molecular structure:



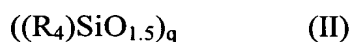
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wherein  $R_1$  is C<sub>1-3</sub> alkyl, preferably methanyl;  $R_2$  is hydrogen atom, C<sub>1-3</sub> alkyl or C<sub>2</sub>-  
 15 10 alkenyl, preferably hydrogen atom, vinyl or methanyl;  $R_3$  is C<sub>1-3</sub> alkyl or phenyl, preferably methanyl or phenyl; the aforesaid silicone compound has molecular weight between 3,500 and 30,000, preferably between 100,000 and 700,000; if calculated by molecular weight, (-Si( $R_1$ )( $R_1$ )O-)<sub>m</sub> accounts for 60 ~ 95% of silicone compound, (-Si( $R_1$ )( $R_2$ )O-)<sub>n</sub> accounts for 0 ~ 10%, (-Si( $R_1$ )( $R_2$ )O-)<sub>o</sub> accounts for 0 ~ 10%, and (-

$\text{Si}(\text{R}_3)(\text{R}_3)\text{O}-)_p$  accounts for 0 ~ 10%, preferably  $(-\text{Si}(\text{R}_1)(\text{R}_1)\text{O}-)_m$  accounts for 85 ~ 95% of silicone compound,  $(-\text{Si}(\text{R}_1)(\text{R}_2)\text{O}-)_n$  accounts for 0 ~ 5%,  $(-\text{Si}(\text{R}_1)(\text{R}_2)\text{O}-)_0$  accounts for 0 ~ 5%, and  $(-\text{Si}(\text{R}_3)(\text{R}_3)\text{O}-)_p$  accounts for 0 ~ 5%.

The aforesaid silicone compound having linear molecular structure is prepared by  
5 copolymerization of silicone monomers under high temperature in the presence of catalyst  
and subsequently having reacted catalyst removed and unreacted monomers and low-  
molecular-weight oligomers removed under high vacuum. Examples of said silicone  
monomers include: cyclic  $(-\text{Si}(\text{CH}_3)(\text{CH}_3)\text{O}-)_3$ ,  $(-\text{Si}(\text{CH}_3)(\text{CH}_3)\text{O}-)_4$ ,  $(-\text{Si}(\text{CH}_3)(\text{CH}_3)\text{O}-)_5$ ,  
 $(-\text{Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2)\text{O}-)_4$ ,  $(-\text{Si}(\text{CH}_3)(\text{H})\text{O}-)_4$ , or similar cyclic monomer mixtures,  
10  $\text{H}_2\text{C}=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$ ,  $\text{H}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{H}$ ,  $\text{PhSiCH}_3(\text{OCH}_3)_2$ ,  
and  $\text{Ph}_2\text{Si}(\text{OCH}_3)_2$ , wherein Ph represents phenyl; the catalyst can be strong acid solution.

The aforesaid silicone release modifier may also be a compound having the  
following cage molecular structure:



15 wherein  $\text{R}_4$  is hydrogen atom or  $\text{C}_{2-10}$  alkenyl, preferably hydrogen atom or vinyl; and  $q$  is  
an integer from 8 to 16.

The aforesaid silicone compound having cage molecular structure is prepared by  
dissolving T-type silicone monomers in organic solvent and undergoing hydrolysis and  
condensation reactions with water and catalyst. After removing the catalyst and water and  
20 condensing the leftover solvent in the resulting reactant, the cage-type silicone compound  
is obtained. Examples of said silicon monomers include  $\text{HSiCl}_3$ ,  $\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$ , and

$\text{Si}(\text{OC}_2\text{H}_5)_4$ ; the aforesaid catalyst can be sulfuric acid, hydrochloride acid, or acetic acid.

The aforesaid compound having cage molecular structure may be acquired on the market, such as SST-V8V01 (poly(vinylsilsesquioxane)-T8) or SST-H8H01 (poly(hydridosilsesquioxane)-T8) from Gelest Inc.

5           The higher the proportion of alkenyl group in the aforesaid release modifier, the easier the release following the application of release agent.

The aforesaid release agent can further comprise a catalyst which comprises of platinum catalyst, sulphuric acid, hydrochloric acid, or acetic acid.

10           The aforesaid release agent can further comprise a proper solvent, such as toluene, n-heptane, methylethyl ketone or composition thereof.

The aforesaid release agent can further comprise proper amount of inhibitor, such as alkynol compound or peroxide to enhance the operation life, i.e. pot life of release agent after mixture.

15           The aforesaid release agent can further contain proper amount of microparticles, such as nanometer grade  $\text{SiO}_2$ ,  $\text{TiO}_2$  or organic polymer particles.

The aforesaid release agent can be further reformulated in consideration of the assisting substrate to be separated to give it greater separation property.

The aforesaid release agent may be spin coated, dip coated or roll coated.

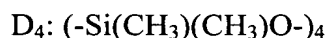
20           The aforesaid assisting substrate comprises glass, chip, Teflon, ceramic or polymer substrate.

The advantages of the present invention are further depicted with the illustration

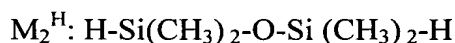
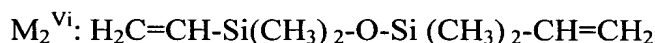


of examples, but the descriptions made in the examples should not be construed as a limitation on the actual application of the present invention.

The symbols of monomers depicted in the examples are defined as follows:



DPh:  $Ph_2Si(OR_2)$ , Ph represents phenyl and R represents  $CH_3$



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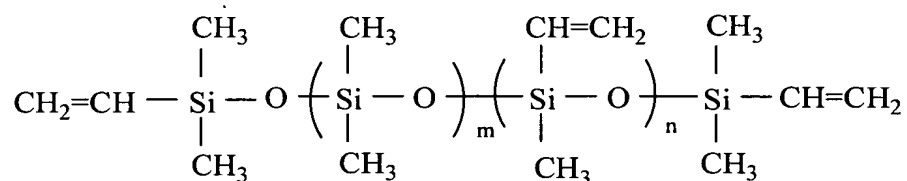
#### EXAMPLE 1 - Preparation of linear release modifier

Weigh 0.43 g of  $D_4^{Vi}$  monomer, 1.86 g of  $M_2^{Vi}$  monomer, 47.71 g of  $D_4$  monomer, and 0.13 g of 0.25 wt% sulfuric acid aqueous solution, and place them in the reaction bottle of rotative reactor. Cap the reaction bottle and turn on the rotative reactor. Raise the temperature of reactor to 80°C and react for 2 hours, then raise the temperature to 130°C and react for 1 hour. After the reaction, drop the temperature and take out the resulting solution and neutralize it with 0.22 g of  $NaHCO_3$ . Agitate the resulting mixture well and remove the salts by centrifugation. Subsequently, place the mixture in evaporator, set the temperature at 180°C, and turn on the vacuum motor. After the atmospheric pressure is below 1.0 torr, remove oligomers of low molecular weight, then raise the temperature to 200°C and maintain for 2 hours until no more distillate comes out. The linear release

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modifier obtained thereof (Sample No. SS-197) has the following structure and predetermined molecular weight of approximately 5000, in which the vinyl content is about 0.1 mol/1000g.



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#### EXAMPLES 2 ~ 6 - Preparation of linear release modifier

Prepare linear release modifiers using the data shown in Table 1 and the same method as that in Example 1. The linear release modifiers obtained thereof are numbered Samples No. SS-198 to SS-202. Sample No. SS-198 to SS-199 have the same structure as that of SS-197; Samples No. SS-200 to SS-202 have the following structure. Other data are illustrated in Table 1.

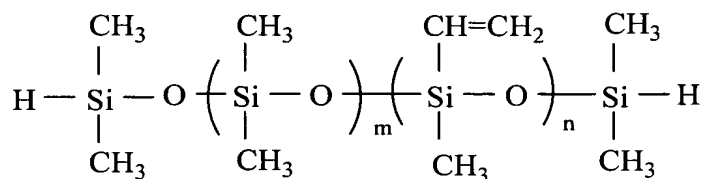


Table 1

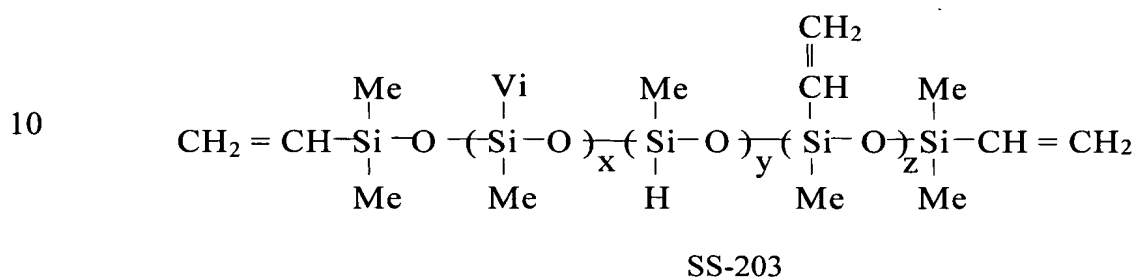
Example No.		1	2	3	4	5	6
Sample No.		SS-197	SS-198	SS-199	SS-200	SS-201	SS-202
Monomer (g)	D <sub>4</sub> <sup>Vi</sup>	0.43	0.86	1.29	0.43	0.86	1.29
	M <sub>2</sub> <sup>Vi</sup>	1.86	1.86	1.86	-	-	-
	M <sub>2</sub> <sup>H</sup>	-	-	-	1.34	1.34	1.34
	D <sub>4</sub>	47.71	47.28	46.85	48.23	47.80	47.37

Catalyst	H <sub>2</sub> SO <sub>4</sub> (0.25wt%)	0.13 g	0.13 g	0.13 g	0.13 g	0.13 g	0.13 g
Neutralizer	NaHCO <sub>3</sub>	0.22 g	0.22 g	0.22 g	0.22 g	0.22 g	0.22 g
Predetermined molecular weight		5000	5000	5000	5000	5000	5000
Vinyl content (mol/1000 g)		0.1	0.2	0.3	0.1	0.2	0.3

### EXAMPLES 7 ~ 13 Preparation of release agent

Take release modifier respectively prepared in Examples 1 ~ 6, No. SS-203 and KE-82-VBS from Shin-Etsu Chemical, toluene, and platinum catalyst CAT-PL-50T diluted to 10% by toluene in an amount as shown in Table 2, and place them in an agitator and mix well. After complete deaeration, the release agents of the present invention are obtained. Measure the viscosity and solid content of the release agents.

Sample No.SS-203 have the following structure:



$$\text{Si-H/Si-CH=CH}_2 = 3.5$$

Molecule weight: 660,000

Apply the prepared release agent to 50μm PET film with 4# wire rod (9 μm) or dip coat on glass, and evaluate its coatability and adhesion.

Evaluation standards for PET coatability: excellent (uniform film thickness and

flat); good (some shrinkage); poor (exhibiting creases).

Evaluation standards for PET adhesion: excellent (no peeling after rubbing 3-5 times with an eraser); good (no peeling after rubbing 1-2 times with an eraser); poor (peel-off immediately after rubbing).

5           Next, subject release agents prepared in Examples 7 – 13 to release testing using Tesa 7475 standard tape and the method described below.

Let the prepared release agent composition stand for 30 minutes, apply it to 50 $\mu$ m PET film with 4# wire rod (9  $\mu$ m). Bake for 60 seconds under 130 $\pm$ 5°C, then cool overnight. Adhere one side of the double-sided 3M tape to a glass slide (5cm  $\times$  10cm  $\times$  0.2cm) and the other side to the aforesaid release-coated PET specimen. Cut the PET specimen to the size of glass slide. Adhere Tesa 7475 standard test tape (2.5 cm  $\times$  13 cm) to the release-coated PET specimen. Stick a release paper strip (2.5 cm  $\times$  15 cm) to the other side of test tape. The release paper strip is hung with a pull ring which is secured by staple. Use a pull tester (Adhesion/ Release Tester AR-1000) to test the release force of  
10           Tesa 7475 standard tape at the pull speed of 12 inch/min. The results are as shown in Table 2.

Next, subject release agents prepared in Examples 7 – 13 to release testing using X7R green tape and the method described below.

Apply release agent to 50 $\mu$ m PET film with 4# wire rod (9  $\mu$ m). Bake for 60  
20           seconds under 130 $\pm$ 5°C, then cool overnight. Use 4# wire rod to apply X7R slurry on the release-coated PET film. Bake under 100 $\pm$ 5°C for 30 seconds, then cool overnight.

Adhere one side of the double-sided 3M tape to a glass slide (5cm × 10cm × 0.2cm) and the other side to release-coated PET film painted with X7R green tape. Cut the PET specimen to the size of glass. Adhere Tesa 7475 standard test tape (2.5 cm × 13 cm) to the surface of X7R. Stick a release paper strip (2.5 cm × 15 cm) to the other side of test tape and hang a pull ring to the release paper strip which is secured by staple. Use a pull tester (Adhesion/ Release Tester AR-1000) to test the release force of X7R green tape at the pull speed of 12 inch/min. The results are as shown in Table 2.

Table 2

Example No. Content(g)	7	8	9	10	11	12	13
SS-197	1						
SS-198		1	1				
SS-199				1			
SS-200					1		
SS-201						1	
SS-202							
SS-203	9	9	9	9	9	9	8.6
KE-82-VBS (25% S.C.)							1.8
Toluene	40	40	40	40	40	40	24
10% CAT-PL-50T	1.2	1.2	1.2	1.2	1.2	1.2	1
Viscosity (CPS)	44	45	45	46	45-46	45	33
Solid content (%)	7.23	7.23	7.23	7.23	7.23	7.23	6.2
PET coatability	good	good	good	good	good	good	good
PET adhesion	good	good	good	good	good	good	excellent
Tesa 7475 standard tape release force	15-26	13-19	12-26	5-7	8-10	7-9	5-7
	18-28	13-20	14-28	5-7	7-9	7-9	5-7
	16-26	14-20	11-24	4-6	7-9	7-9	5-7
Avg. (g/inch)	21±5	17±3	19±7	6±1	7±1	8±1	6±1
X7R green tape release force	2.8-3.2	2.8-3.2	2.7-3.2	2.7-3.2	2.7-3.2	3.0-3.3	2.2-2.5
	2.7-3.1	2.7-3.2	2.7-3.2	3.0-3.3	2.7-3.2	3.0-3.5	2.2-2.4

	2.6-3.0	2.7-3.2	2.7-3.2	2.8-3.3	2.7-3.2	2.9-3.4	2.2-2.5
Avg. (g/in)	2.9±0.2	3.0±0.2	2.9±0.3	3.0±0.3	3.0±0.3	3.2±0.2	2.4±0.2

As shown in Table 2, the PET coatabilities of release agents prepared in Examples 7-13 are good where some shrinkage occurred; the PET adhesions in Examples 7-12 are also good, whereas the release agent in Example 13 exhibited good PET adhesion. By Tesa 7475 standard tape test results, the release force of release agents in Examples 10-13 was markedly smaller than that of release agents in Examples 7-9, indicating that the release agents in Examples 10 –13 have better releasability. By the X7R green tape test results, the release agent in Example 13 displayed the smallest release force, which however differs little from that of release agents in Examples 7 – 12.

#### EXAMPLE 14 Process of non-substrate liquid crystal display element

The manufacturing of first assisting substrate 10 is carried out first. As shown in Fig. 1A, apply release agent prepared in example 10 on first assisting substrate 10 to form a release agent layer 20. Next, apply photosensitive material 30 on release agent layer 20 as shown in Fig. 1B; as shown in Fig. 1C, irradiate 365nm UV light on photosensitive material 30 to form a cured photosensitive material layer 30'; as shown in Fig. 1D, fabricate electrode pattern 40 on cured release agent layer 30'.

Next carry out the manufacturing of second assisting substrate 11. As shown in Fig. 2A ~ 2C, the steps in the process are the same as those in the manufacturing of first assisting substrate: first apply release agent layer 21 on second assisting substrate 11 as

shown in Fig. 2A. Next apply photosensitive material 31 on release agent layer 21 as shown in Fig. 2B, then polymerize and cure the photosensitive material with UV light to form cured photosensitive material layer 31' as shown in Fig. 2C. Then fabricate electrode pattern 41 on cured photosensitive material layer 31' as shown in Fig. 2D and  
5 coat alignment layer 50. Subsequently apply photo-polymerizable mixture 60, which contains photosensitive material and liquid crystal material on alignment layer 50 as shown in Fig. 2E.

Fig. 3 depicts the process of assembling first assisting substrate 10 and second assisting substrate 11. As shown in Fig. 3A, place first assisting substrate 10 upside down  
10 over second assisting substrate 11 and align, and then expose the two substrates to light through photomask (not shown in the figure); after exposure, the photo-polymerizable mixture 60 forms a plurality of polymer walls 70 which adjoin the first assisting substrate 10 and the second assisting substrate 11, and induce the phase-separation between liquid crystal and photosensitive material with polymer walls 70 surrounding the liquid crystal  
15 80 as shown in Fig. 3B; next, peel off first assisting substrate 10, second assisting substrate 11, and their respective release agent layer 20 and 21 as shown in Fig. 3C; finally, a non-substrate liquid crystal display element 100 is obtained as shown in Fig. 3D.